

### Remarks

Claims 1 to 28 inclusive are being prosecuted.

By this amendment claims 4 and 5 have been amended to define the preferred dispersion as discussed in the application and hereinbelow.

Reconsideration of the rejects of the claims of the this application in view of the cited references is respectfully requested in the light of the following review and analysis of the citations and their teaching relative to what is taught and claimed herein.

1. 35 USC § 102 Anticipation of the Claims and/or 35 USC § 103 (a) as obvious in view of Koblinski et al.

The objections are based on four references. A review of Applicant's understanding of each of the references and their relevance to the present invention follows

- a) Van Looij describes a nickel on alumina catalyst for methane steam reforming using very high nickel loadings. While crystallite sizes are reported in this patent no specific data about metal dispersion is given. Our calculations (based on the standard procedure for such calculations show as pointed out in the previous response that in the van Looij's catalyst a much higher metal dispersion ( $1 \text{ m}^2 \text{ Ni/m}^2$  support) is used versus the one considered desirable in our catalyst ( $0.14 \text{ m}^2 \text{ Ni/m}^2$  for an alumina support). Claim 1 as currently pending defines the dispersion as limited to  $0.2 \text{ m}^2 \text{ nickel/m}^2$  support.. Claim 1 defines "*and a dispersion on said support element of no more than 0.2 square meter of exposed nickel/ square meter of support surface*" Metal dispersion close to  $1 \text{ m}^2 \text{ Ni/m}^2$  of support, as proposed by van Looij et al., promotes crystallite agglomeration during the successive reaction-oxidation cycles.

The problems with nickel crystallite agglomeration under the conditions of dry reforming with repeated reaction and regenerations are described in this application (see page 9 line 11 +)

*"The present invention is based on finding that the crystallite size of the metal (nickel Ni) crystallites and the distribution of these crystallites are particularly important for the effectiveness of the catalyst in the reforming process and in the rejuvenation of the catalyst after use minimizing agglomeration of the crystallites the growth of the crystallite size during the rejuvenation stage."*

and claim 1 specifically requires that the

*"said catalyst being capable of withstanding at least 6 catalyst regenerations without significantly inhibiting it's catalytic activity in said reforming process"*

Thus, it is submitted the van Looij's catalyst with high metal dispersion of  $1.04 \text{ m}^2 \text{ Ni/m}^2$  of support is inadequate in meeting the requirements of the present invention and does not in any way lead one to the present invention.

- b) Kobylinski et al describes a synthesis gas conversion catalyst, not a reforming catalyst, suggesting nickel-loading levels between 1 to 50wt% with a vague reference to "*small crystallites*". No other discussion about crystallite size or metal dispersion is provided. Thus, there is no possible way of establishing if the catalyst design parameters of Kobylinski met those required for a suitable methane dry reforming catalyst. Kobylinski et al is silent about those issues and as a result there is no reason to believe that they understood the need of introducing and closely adhering to key design principles for the preparation of a suitable catalyst for dry methane reforming. Thus there is no teaching in this reference that would in any way lead one toward the present invention.
- c) Viltard et al patent teaches the application of nickel catalysts to benzene hydrogenation to reduce the benzene content and thus the toxicity of gasoline. The use of Ni as a catalyst for this purpose is a well known (i.e. for use in hydrogenation-dehydrogenolysis catalyst). Viltard et al discloses an extremely wide range catalyst for hydrogenation of hydrocarbons based on nickel supported on a number of materials including alumina, silica-alumina, silica, zeolites, etc. The recommended loadings levels for these catalysts are extremely broad defined as in the 5% to 70% range with nickel crystallites described as smaller than 100A and preferably smaller than 80A. These broad teachings provide no insight into catalysts for applicant's purpose i.e. as defined in claim 1

*"A regenerable Nickel (Ni) catalyst for a hydrocarbon reforming process"*

The fact that the wide range of nickel based catalyst are suitable for hydrogenation and dehydrogenation reactions of hydrocarbons does not mean that such catalyst will be useful for applicants claimed purpose. Considering the theories of operation of the different processes involved and the principle of microscopic reversibility it is clear that performance for methane dry reforming is not predicable. Methane reforming of the present invention is

driven by a completely different mechanism than that for hydrogenation and dehydrogenation. In the methane reforming process of the present invention where reagents, methane and  $\text{CO}_2$ , are strongly adsorbed on different catalytic sites (e.g. the  $\text{CO}_2$  on the nickel and the  $\text{CH}_4$  on the alumina or zeolite support). See El Solh et al, Ind.Engng.Chem Res. Vol. 42, 2507-2512, 2003 copy attached.

In addition and regarding the possible use of zeolites as a support, no reference is given in Viltard et al to a specific type of zeolite. Proper selection of the zeolite strongly affects both nickel crystal size and metal dispersion which is important for the purposes of the present invention. Viltard et al does not provide any teaching about selecting a specific type of zeolite to aid in preventing nickel redispersion and agglomeration, thus there is no reason to believe that Viltard et al appreciate the important facts behind nickel crystallite formation for a good dry reforming catalyst.

- d) Jarosch et al. paper describes an early contribution of some of the inventors of the present invention and provides a broad discussion of nickel on alumina catalyst for steam methane reforming. There is no discussion of the specific catalyst of the present invention, in fact at the time of that paper there could be not discussion of the present invention as it had yet to be invented.

In summary, none of the above discussed patents (a to d) refers to nickel supported catalyst for a hydrocarbon reforming process, and none elucidate the key parameters and key requirements for catalysts of the present invention which must undergo periodic reaction and regeneration cycles. Applicant has done much more than simple optimization, as suggested by the in the Office Action.

2. "No differences is seen between the crystallite of Kobylinski et al and those of the applicant".

As stated in the previous section Kobylinski et al describes a synthesis gas conversion catalyst, not a reforming catalyst, suggesting nickel loadings between 1 to 50wt% with a vague reference to "small crystallites". There is no specific discussion about crystallite size or metal dispersion. Thus, Kobylinski et al did not disclose key parameters for catalysts preparation and there is no way to establish if this catalyst is suitable for methane dry reforming. Furthermore the catalyst structure taught by Kobylinski et al does not have the physical characteristics of the catalyst

defined in Claim 1 of this application. Thus, it is submitted, this patent has little or no significance with respect to the invention claimed.

3. *"It would have been obvious.. to have performed the incipient ness method various times until achieving the desired small crystal size.."*

It is believed that this comment ignores the fact that the crystallite formation mechanism of this invention is closely related to a "saturation" condition by which crystallites are formed.

As is known once the support is impregnated via incipientness wetness, to achieve a targeted catalyst loading, catalyst particles are dried. It is under these conditions of water evaporation that "saturation" in the impregnating solution is reached. At "saturation" crystallite seeds are formed and grow in the impregnating solution until water is completely evaporated and crystallites settle on the surface of the support. Following this, the  $\text{NiNO}_3$  is decomposed first into  $\text{NiO}$  via calcination and later on reduced to  $\text{Ni}$  (see page 11 of this application). It should be noted that reduced nickel crystallites, formed during a previous impregnation cycle and laying on the catalyst surface as nickel (zero valence) crystallites, play no role as seeds for forming larger crystals in subsequent cycles of impregnation.

Thus, a multistep catalyst impregnation developed with a  $[\text{Ni}]/n$  solution concentration, with  $[\text{Ni}]$  being the nickel solution concentration used in a single impregnation step and "n" the number of impregnations steps, always helps forming small crystallites with a narrow size distribution. While in principle and to get tiny crystallites, for a given nickel loading and controlled metal dispersion, one should use many impregnation cycles, in practice one is limited to a set number of impregnations (e.g. 4 impregnation steps each of them with impregnating solutions of a  $1/4$  concentration with respect to the one employed in a single impregnation step).

In summary, and as discussed above, the multistep process as specified in the claims i.e.

*"by a several incipient wetness steps process incorporating a plurality of Ni impregnation cycles"*

(as defined in claim 1 and 23 the only two independent claims in the application) is very essential vis-à-vis of the invention i.e. a for methane reforming catalyst having small crystallite sizes and high metal dispersion as taught by the present invention.

**4. "Discovering the optimum value it depends on whether or not was obvious base on the prior art or whether the new invention has identified a new target"**

The discovery of the best catalyst for methane reforming is not a simple matter of changing parameters and optimizing existing formulations. The invention leading to the best catalyst for methane reforming requires the application of important principles of catalyst design:

- The identification and selection of combined values of key parameters (nickel loading, crystallite size and metal dispersion) not described in previous patents, leading to the formulation of reforming catalysts sustaining the repeated cycles of reaction and regeneration with no crystallite agglomeration and high performance.
- A multiple step process of impregnation, not described in previous patents, controlling the formation of the nickel crystallites at "saturation" conditions.

It is submitted that the claims clearly distinguish the present invention from the prior art and that this application is in condition for Allowance and such action is respectfully requested.

Respectfully submitted,



C.A. Rowley Reg. No. 20,781  
Agent for Applicant

Date: June 16, 2003  
Telephone (613) 398 1409

**Certificate of Transmission**

I hereby certify that this correspondence ( 18 pages) is being facsimile transmitted to the United States Patent and Trademark Office (Fax no. (703) 872 9310) on June 16, 2003

(Date)

Typed name of the person signing this certificate

Signature

C.A. Rowley

